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<b>(21) International Application Number:</b> PCT/US93/08151 <b>(22) International Filing Date:</b> 30 August 1993 (30.08.93)  <b>(30) Priority data:</b> 92870138.2 1 September 1992 (01.09.92) EP <i>(34) Countries for which the regional or international application was filed:</i> BE et al. 93200460.9 18 February 1993 (18.02.93) EP <i>(34) Countries for which the regional or international application was filed:</i> BE et al.  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).		<b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN DIJK, Paul [BE/BE]; Leuvensebaan 226, B-2580 Putte (BE). VEGA, Jose, Luis [ES/BE]; Nieuwelaan 121, B-1853 Strombeek-Bever (BE). FRANCE, Paul, Amaat, Raymond, G. [BE/BE]; Patrijzenlaan 36 Bus 2, B-3010 Kessel-Lo (BE).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).  <b>(81) Designated States:</b> AU, BB, BG, BR, BY, CA, CZ, FI, HU, JP, KP, KR, KZ, LK, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SK, UA, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR MAKING HIGH DENSITY GRANULAR DETERGENT AND COMPOSITIONS MADE BY THE PROCESS  <b>(57) Abstract</b>  A process in which the bulk density of a particulate detergent material is increased starting from an initial bulk density of at least 600 g/l, by spraying a liquid onto the particles and dusting with a fine powder in one or more rotating drum(s) or mixer(s), characterised in that the particulate detergent material initially has a mean particle size greater than 400 micrometers, and that the increase in the mean particle size during the process is not greater than 60 %. The invention also discloses a detergent composition having excellent dispensing and dissolving properties.		

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Process for Making High Density Granular Detergent  
and Compositions made by the Process

BACKGROUND OF THE INVENTION

There is a trend amongst commercially available granular detergents towards higher bulk densities. This gives benefits both for consumer convenience and for reduction of packaging materials.

Many of the prior art attempts to move in this direction have met with problems of poor solubility properties arising from low rate of dissolution or the formation of gels. A consequence of this in a typical washing process can be poor dispensing of the product, either from the dispensing drawer of a washing machine, or from a dosing device placed with the laundry inside the machine. This poor dispensing is often caused by gelling of particles which have high levels of surfactant upon contact with

water. The gel prevents a proportion of the detergent powder from being solubilised in the wash water which reduces the effectiveness of the powder. Another adverse consequence arises even if the powder is well dispensed and dispersed in the washing water if it does not dissolve rapidly. The wash cycle has a limited duration during which the detergent can act upon the laundry. If the cleaning action is delayed because the powder is slow to dissolve, this, too, will limit the effectiveness of the powder.

The process engineer and formulator have frequently found that the need for good dispensing and the need for good dissolution rate have placed conflicting demands upon them. The solution has generally been to find a compromise which gives adequate dispensing and adequate dissolution rate. For example, poor dispensing of high bulk density granular detergents is often associated with surfactant rich particles having a high specific surface area, either due to high porosity or a small particle size (especially "fines"). However, decreasing the porosity and/or increasing the average particle size cause the dissolution rate to decrease.

Various methods for increasing bulk density are described in the prior art - in many cases by using processes which densify spray dried powders.

EP 184794 published on 18th June, 1986 (Henkel) describes a process of loading an adsorbant carrier with nonionic surfactant in a Loedige mixer which increases the bulk density. The carrier is typically prepared by spray drying.

EP 327963 published on 16th August, 1989 (Henkel) describes a basic post tower densification process in which the spray dried component is pulverised prior to reagglomerating in a granulation step.

EPA 367339 published on 9th May, 1990 (Unilever) describes a two-stage agglomeration process.

Even more recently processes have been developed whereby a spray drying step has been completely eliminated. This has been achieved by making particles which comprise surfactants and builders by, for example extrusion or agglomeration of viscous pastes.

However all of the prior art processes suffer either from the presence of very small particles (fines) which tend to gel and cause poor dispensing properties, or from the presence of large, low porosity particles which overcome the dispensing problem, but which are slow to dissolve in the wash process.

It is the aim of the present invention to provide a detergent composition that has three key properties:

- i) a high bulk density
- ii) good dispensing properties
- iii) and dissolves rapidly.

This has been achieved by firstly dry mixing most (or all) of the components of the finished detergent composition in a granular form, and subsequently increasing the bulk density by spraying on a liquid into one or more rotating drums or mixers.

It is an essential feature of the present invention that the initial particles must be granular (not dust), and they are not passed through a pulverisation step. This is key to achieving the benefits in dispensing properties.

It is also an essential feature of the present invention that the mean particle size of the granular particles of

the finished product should not be so great that the rate of dissolution is slow.

#### SUMMARY OF THE INVENTION

A process in which the bulk density of a particulate detergent material is increased starting from an initial bulk density of at least 600g/l, by spraying a liquid on to the particles and dusting with a fine powder in one or more rotating drum(s) or mixer(s),

characterised in that the particulate detergent material initially has a mean particle size greater than 400 micrometers, and that the increase in the mean particle size during the process is not greater than 60%.

The invention also discloses a detergent composition having excellent dispensing and dissolving properties.

#### DETAILED DESCRIPTION OF THE INVENTION

It is the aim of the present invention to provide a detergent composition that has three key properties:

- i) a high bulk density
- ii) good dispensing properties
- iii) and dissolves rapidly.

This has been achieved by firstly dry mixing most (or all) of the components of the finished detergent composition in a granular form, and subsequently increasing the bulk density by spraying on a liquid into one or more rotating drums or mixers.

The required properties are achieved by mixing most (or all) of the detergent components in the form of granular powders, in order to give a mixed particulate material having a defined mean particle size and bulk density. The bulk density is then further increased by spraying a liquid, and dusting with a finely particulate flow aid in one or more rotating drums or mixers in order to "round off" the particles by filling pores and surface irregularities.

It is an essential feature of the present invention that the powder at the inlet of the rotating drums/mixers is in a granular form (with little or no fines), and not pulverised as a dust. This feature gives the dispensing benefits (because the absence of fine powder/dust avoids gel formation upon contact with water).

#### Preparation of the Mix of Granular Components

The granular components used in the present invention are made from a wide range of ingredients useful for their detergency which are chosen according to the demands of the product formulator. Suitable ingredients are described below.

#### Surfactants

Surfactants are selected from the group consisting of anionic, zwitterionic, ampholytic and cationic surfactants, and mixtures thereof. Anionic surfactants are preferred. Surfactants useful herein are listed in U.S. Pat. No. 3,664,961, Norris, issued May 23, 1972, and in U.S. Pat. No. 3,919,678, Laughlin et al., issued Dec. 30, 1975. Useful cationic surfactants also include those described in U.S. Pat. No. 4,222,905, Cockrell, issued Sept. 16, 1980, and in U.S. Pat. 4,239,659, Murphy, issued Dec. 16, 1980. However, cationic surfactants are generally less compatible

with the aluminosilicate materials herein, and thus are preferably used at low levels, if at all, in the present compositions. The following are representative examples of surfactants useful in the present compositions.

Water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium, ammonium, and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

Useful anionic surfactants also include the water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols ( $C_8$ - $C_{18}$  carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the sodium and potassium alkyl benzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099 and 2,477,383.

Other anionic surfactants herein are the sodium alkyl glyceryl ether sulfonates, especially those ethers of

higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; watersoluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety.

Also useful are the sulphonation products of fatty acid methyl esters containing a alkyl group with from 10 to 20 carbon atoms. Preferred are the C16-18 methyl ester sulphonates (MES)

Water-soluble nonionic surfactants are also useful as secondary surfactant in the compositions of the invention. Such nonionic materials include compounds produced by the condensation of alkylene oxid groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the

polyoxyalkylene group which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Suitable nonionic surfactants include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 16 carbon atoms, in either a straight chain or branched chain configuration, with from about 4 to 25 moles of ethylene oxide per mole of alkyl phenol.

Preferred nonionics are the water-soluble condensation products of aliphatic alcohols containing from 8 to 22 carbon atoms, in either straight chain or branched configuration, with from 4 to 25 moles of ethylene oxide per mole of alcohol. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 25 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide.

Other useful nonionic surfactants are based upon natural renewable sources such as glucose. Alkyl polyglucoside (APG), preferably those containing from 10 to 20 carbon atoms and an average of from 1 to 4 glucose groups. Also useful are nonionic surfactants based on glucose amides which contain an alkyl group with from 10 to 20 carbon atoms, for example tallow N-methyl glucamine.

Polyhydroxy fatty acid amides may be produced by reacting a fatty acid ester and an N-alkyl polyhydroxy amine. The preferred amine for use in the present invention is  $N-(R_1)-CH_2(CH_2OH)_4-CH_2-OH$  and the preferred ester is a C12-C20 fatty acid methyl ester. Most preferred

is the reaction product of N-methyl glucamine with C12-C20 fatty acid methyl ester.

Methods of manufacturing polyhydroxy fatty acid amides have been described in WO 92 6073, published on 16th April, 1992. This application describes the preparation of polyhydroxy fatty acid amides in the presence of solvents. In a highly preferred embodiment of the invention N-methyl glucamine is reacted with a C12-C20 methyl ester. It also says that the formulator of granular detergent compositions may find it convenient to run the amidation reaction in the presence of solvents which comprise alkoxylated, especially ethoxylated (EO 3-8) C12-C14 alcohols (page 15, lines 22-27). This directly yields nonionic surfactant systems which are preferred in the present invention, such as those comprising N-methyl glucamide and C12-C14 alcohols with an average of 3 ethoxylate groups per molecule.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be either straight or branched chain and wherein one of

the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium phosphonium, and sulfonium compounds in which one of the aliphatic substituents contains from about 8 to 18 carbon atoms.

Particularly preferred surfactants herein include tallow alkyl sulfates; coconutalkyl glyceryl ether sulfonates; alkyl ether sulfates wherein the alkyl moiety contains from about 14 to 18 carbon atoms and wherein the average degree of ethoxylation is from about 1 to 4; olefin or paraffin sulfonates containing from about 14 to 16 carbon atoms; alkyldimethylamine oxides wherein the alkyl group contains from about 11 to 16 carbon atoms; alkyldimethylammonio propane sulfonates and alkyldimethylammonio hydroxy propane sulfonates wherein the alkyl group contains from about 14 to 18 carbon atoms; soaps of higher fatty acids containing from about 12 to 18 carbon atoms; condensation products of C9-C15 alcohols with from about 3 to 8 moles of ethylene oxide, and mixtures thereof.

Useful cationic surfactants include water-soluble quaternary ammonium compounds of the form  $R_4R_5R_6R_7N^+X^-$ , wherein  $R_4$  is alkyl having from 10 to 20, preferably from 12-18 carbon atoms, and  $R_5$ ,  $R_6$  and  $R_7$  are each  $C_1$  to  $C_7$  alkyl preferably methyl;  $X^-$  is an anion, e.g. chloride. Examples of such trimethyl ammonium compounds include  $C_{12}$ - $C_{14}$  alkyl trimethyl ammonium chloride and cocalkyl trimethyl ammonium methosulfate.

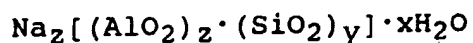
Specific preferred surfactants for use herein include: alpha-olefin sulphonates; triethanolammonium  $C_{11}$ - $C_{13}$  alkylbenzene sulfonate; alkyl sulfates, (tallow, coconut,

palm, synthetic origins, e.g. C<sub>45</sub>, etc.); sodium alkyl sulfates; methyl ester sulphonate; sodium coconut alkyl glyceryl ether sulfonate; the sodium salt of a sulfated condensation product of a tallow alcohol with about 4 moles of ethylene oxide; the condensation product of a coconut fatty alcohol with about 6 moles of ethylene oxide; the condensation product of tallow fatty alcohol with about 11 moles of ethylene oxide; the condensation of a fatty alcohol containing from about 14 to about 15 carbon atoms with about 7 moles of ethylene oxide; the condensation product of a C<sub>12</sub>-C<sub>13</sub> fatty alcohol with about 3 moles of ethylene oxide; 3-(N,N-dimethyl-N-coconutalkylammonio)-2-hydroxypropane-1-sulfonate; 3-(N,N-dimethyl-N-coconutalkylammonio)-propane-1-sulfonate; 6- (N-dodecylbenzyl-N,N-dimethylammonio). hexanoate; dodecyldimethylamine oxide; coconutalkyldimethylamine oxide; and the water-soluble sodium and potassium salts of coconut and tallow fatty acids.

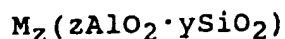
#### Detergency Builders

Any compatible detergency builder or combination of builders or powder can be used in the process and compositions of the present invention.

The detergent compositions herein can contain crystalline aluminosilicate ion exchange material of the formula



wherein z and y are at least about 6, the molar ratio of z to y is from about 1.0 to about 0.4 and z is from about 10 to about 264. Amorphous hydrated aluminosilicate materials useful herein have the empirical formula



wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2 and y is 1, said

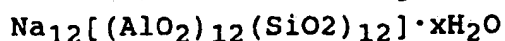
material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of  $\text{CaCO}_3$  hardness per gram of anhydrous aluminosilicate. Hydrated sodium Zeolite A with a particle size of from about 1 to 10 microns is preferred.

The aluminosilicate ion exchange builder materials herein are in hydrated form and contain from about 10% to about 28% of water by weight if crystalline, and potentially even higher amounts of water if amorphous. Highly preferred crystalline aluminosilicate ion exchange materials contain from about 18% to about 22% water in their crystal matrix. The crystalline aluminosilicate ion exchange materials are further characterized by a particle size diameter of from about 0.1 micron to about 10 microns. Amorphous materials are often smaller, e.g., down to less than about 0.01 micron. Preferred ion exchange materials have a particle size diameter of from about 0.2 micron to about 4 microns. The term "particle size diameter" herein represents the average particle size diameter by weight of a given ion exchange material as determined by conventional analytical techniques such as, for example, microscopic determination utilizing a scanning electron microscope. The crystalline aluminosilicate ion exchange materials herein are usually further characterized by their calcium ion exchange capacity, which is at least about 200 mg equivalent of  $\text{CaCO}_3$  water hardness/g of aluminosilicate, calculated on an anhydrous basis, and which generally is in the range of from about 300 mg eq./g to about 352 mg eq./g. The aluminosilicate ion exchange materials herein are still further characterized by their calcium ion exchange rate which is at least about 2 grains  $\text{Ca}^{++}$ /gallon/minute/gram/gallon of aluminosilicate (anhydrous basis), and generally lies within the range of from about 2 grains/gallon/minute/gram/gallon to about 6 grains/gallon/minute/gram/gallon, based on calcium ion hardness. Optimum aluminosilicate for builder purposes

exhibit a calcium ion exchange rate of at least about 4 grains/gallon/minute/gram/gallon.

The amorphous aluminosilicate ion exchange materials usually have a  $Mg^{++}$  exchange of at least about 50 mg eq.  $CaCO_3/g$  (12 mg  $Mg^{++}/g$ ) and a  $Mg^{++}$  exchange rate of at least about 1 grain/gallon/minute/gram/gallon. Amorphous materials do not exhibit an observable diffraction pattern when examined by Cu radiation (1.54 Angstrom Units).

Aluminosilicate ion exchange materials useful in the practice of this invention are commercially available. The aluminosilicates useful in this invention can be crystalline or amorphous in structure and can be naturally occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is discussed in U.S. Pat. No. 3,985,669, Krummel et al., issued Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite B, and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula



wherein x is from about 20 to about 30, especially about 27 and has a particle size generally less than about 5 microns.

The granular detergents of the present invention can contain neutral or alkaline salts which have a pH in solution of seven or greater, and can be either organic or inorganic in nature. The builder salt assists in providing the desired density and bulk to the detergent granules herein. While some of the salts are inert, many of them also function as detergency builder materials in the laundering solution.

Examples of neutral water-soluble salts include the alkali metal, ammonium or substituted ammonium chlorides, fluorides and sulfates. The alkali metal, and especially sodium, salts of the above are preferred. Sodium sulfate is typically used in detergent granules and is a particularly preferred salt. Citric acid and, in general, any other organic or inorganic acid may be incorporated into the granular detergents of the present invention as long as it is chemically compatible with the rest of the agglomerate composition.

Other useful water-soluble salts include the compounds commonly known as detergent builder materials. Builders are generally selected from the various water-soluble, alkali metal, ammonium or substituted ammonium phosphates, polyphosphates, phosphonates, polyphosphonates, carbonates, silicates, borates, and polyhyroxysulfonates. Preferred are the alkali metal, especially sodium, salts of the above.

Specific examples of inorganic phosphate builders are sodium and potassium tripolyphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Examples of polyphosphonate builders are the sodium and potassium salts of ethylene diphosphonic acid, the sodium and potassium salts of ethane 1-hydroxy-1,1-diphosphonic acid and the sodium and potassium salts of ethane, 1,1,2-triphosphonic acid. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

Examples of nonphosphorus, inorganic builders are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicate having a molar ratio of  $\text{SiO}_2$  to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about

2.4. Layered silicates of the type manufactured by Hoechst AG, Frankfurt, Germany and sold under the trade name SKS-6 are also useful in the present invention.

As mentioned above chemical ingredients normally used in detergents such as zeolite, carbonate, silica, silicate, citrate, phosphate, perborate, percarbonate etc. and process acids such as starch, can be used in preferred embodiments of the present invention.

#### Polymers

Also useful are various organic polymers, some of which also may function as builders to improve detergency. Included among such polymers may be mentioned sodium carboxy-lower alkyl celluloses, sodium lower alkyl celluloses and sodium hydroxy-lower alkyl celluloses, such as sodium carboxymethyl cellulose, sodium methyl cellulose and sodium hydroxypropyl cellulose, polyvinyl alcohols (which often also include some polyvinyl acetate), polyacrylamides, polyacrylates and various copolymers, such as those of maleic and acrylic acids. Molecular weights for such polymers vary widely but most are within the range of 2,000 to 100,000.

Polymeric polycarboxyate builders are set forth in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. Such materials include the water-soluble salts of homo-and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylenemalononic acid.

#### Optionals

Other ingredients commonly used in detergent compositions can be included in the compositions of the present invention. These include flow aids, color

speckles, bleaching agents and bleach activators, suds boosters or suds suppressors, antitarnish and anticorrosion agents, soil suspending agents, soil release agents, softening clays, dyes, fillers, optical brighteners, germicides, pH adjusting agents, nonbuilder alkalinity sources, hydrotropes, enzymes, enzyme-stabilizing agents, chelating agents and perfumes.

Optical brighteners may be incorporated either directly into one (or more) of the granular components, or a solution or slurry of optical brightener may be sprayed into the rotating drum or mixer during the process of the present invention.

Particulate suds suppressors may also be incorporated in the finished composition by mixing according to the present invention. Preferably the suds suppressing activity of these particles is based on fatty acids or silicones.

#### Mixing

The granular components may be prepared and mixed by any conventional means. Typically the mixing process may be carried out continuously by metering each component by weight on to a moving belt, and blending them in a rotating drum or mixer. The mean particle size of the mixed granular components must be greater than 400 micrometers, and the bulk density must be greater than 600 g/l.

In order to achieve these physical characteristics of the granular component mix, and in order to maintain the dispensing benefits of the present invention, it is preferred that the individual granular components are prepared by processes other than spray drying such as agglomeration, compaction, encapsulation etc. One particularly preferred process of agglomerating high active surfactant pastes with builders and other powders is

described in the Applicants' co-pending European Application No. EPA 510746 published on 28th October 1992. It is preferred that little or none of the granular components is prepared by spray drying of slurries comprising organic surfactants. Such spray dried components generally require a pulverisation step in order to prepare a high bulk density component. In general it is preferred that there is no granular component which has been prepared by spray drying, and which comprises an organic surfactant, which is present at a level of greater than 10% by weight of the finished product.

#### The Drum/Mixer Process

The process of the present invention is carried out in one or more drum(s) or mixer(s) in which the bulk density of the product is increased without losing the benefits of good dispensing properties and rapid rate of dissolution

Without wishing to be bound by theory the granular particles are rolled within the drum/mixer in the "wet" state causing them to become rounded and increasingly regular in shape (ie more spherical) and particle size. This results in a finished composition with a density of at least 750 g/l, preferably greater than 800 g/l.

Suitable equipment includes various rotating drums or mixers with a rotating shaft, such as ribbon blenders or low shear mixers supplied by Lödige Maschinenbau GmbH, Paderborn, Germany (especially those mixers supplied under the Trade Mark Loedige KM). Such a low shear mixer comprises mixing tools, often of the "ploughshare" type mounted on to the rotating shaft. If a low shear mixer is used, the rotational speed of the shaft should be less than 250 rpm.

It is preferred that the liquid sprayed on to the mix of granular components comprises nonionic surfactant. Useful nonionic surfactants have been described hereinabove.

Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 9 to 15 carbon atoms with from about 4 to 25 moles of ethylene oxide per mole of alcohol; and condensation products of propylene glycol with ethylene oxide.

Other liquid ingredients may also be sprayed on to the mix of granular components either separately or premixed.

Typically perfume and slurries of optical brightener may be sprayed. Although any optical brightener may be added in this way, it has been found that Colour Index Fluorescent Brightener number 351 (as published by the Society of Dyers and Colourists and the American Association of Textile Chemists and Colourists) gives particular benefits of colour stability.

High Speed Cutters or Choppers may be advantageously used in order to prevent large balls of product from forming when wet, but pulverisation of the powders (which could occur when they are dry) should be avoided. The high speed cutters or choppers may be mounted on a shaft which is oriented radially with respect to the wall of the mixer, and preferably the shaft rotates at a speed greater than 1000rpm.

The process must be differentiated from a more conventional agglomeration process. This can clearly be seen by observing the increase in mean particle size from beginning to end of the process. In the present invention, the mean particle size does not increase by more than about 60% of the initial mean particle size.

Preferably it does not increase by more than 40%, and more preferably it does not increase by more than 20% of the initial mean particle size.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the theoretical aperture size through which 50% by weight of the sample would pass.

According to the present invention finely divided flow aid (such as zeolites, carbonates, silicates, silicas) is added to the mix of granular components, preferably towards the end of the process. These dusting agents are the only components which are added as a dust. It is therefore particularly important that the flow aids selected do not gel upon contact with water (as some forms of finely divided silicates would). This careful selection of finely divided flow aid enables the bulk density to be further increased without losing the benefits of the good dispensing properties.

#### Finished Compositions

The present invention provides a method of making detergent compositions with very high bulk densities, which also have the characteristics of excellent dispensing properties and a rapid rate of dissolution. This method is very flexible with regard to the formulations that can be processed. Indeed any chemical that can be incorporated into a granular particle may be incorporated into a high bulk density composition by the process defined hereinabove.

A particularly preferred embodiment of the present invention is a composition which has a bulk density of at least 750g/l, preferably at least 800g/l which comprises;

- a) From 5% to 20% of organic surfactant
- b) From 5% to 20% of sodium aluminosilicate

and which has a dispensing residue of less than 30% when:

a 150g sample of the detergent composition is poured into a drawer of a Zanussi (TM) shower-type dispenser, and 4 litres of water at a temperature of 20°C is passed through the said drawer from the nozzles of the dispenser at a rate of 2 litres/minute, after which the portion of the detergent composition remaining in said dispensing drawer is weighed, and the resulting weight expressed as a percentage of the initial 150g sample and averaged over at least 5 repetitions of the test, the resulting percentage being the dispensing residue;

and which has a rate of dissolution of the detergent composition which is at least 50% of the sulphate/sulphonate salts passing into solution in less than 3 minutes when a 10g sample is dissolved in 1 litre of distilled water at a temperature of 20°C in a 1 litre Sotax cup, and with a Sotax stirring propellor no. 3990-2 rotating at 200rpm about a vertical axis, the bottom of the said stirring propellor being located 33mm above the bottom of the cup.

Details of the recommended test methods are given in Section B.

Most preferred compositions comprise mixed anionic surfactant systems having a Krafft temperature less than 40°C in order to achieve a good rate of dissolution at mean particle size of 550-750micrometers.

Furthermore most preferred compositions are nil-phosphate and nil-linear alkyl benzene sulphonate (nil-LAS) for environmental reasons.

EXAMPLESEXAMPLE I

A mixture of granular raw materials is prepared according to the following composition :

	<u>% by weight</u>
Anionic surfactant agglomerate	30.0
Layered silicate compacted granule	17.7
Percarbonate	24.7
TAED agglomerate	9.2
Suds suppressor agglomerate	2.2
Perfume encapsulate	0.2
Granular soil release polymer	0.6
Granular dense soda ash	8.6
Granular acrylic-maleic copolymer	3.2
Enzymes	3.6
	-----
	100

The anionic surfactant agglomerate is prepared by agglomeration of a 78% active C45AS/C35A<sub>3</sub>S 80:20 paste and a phosphonate solution (35%) onto a powder mixture containing zeolite / carbonate / MgSO<sub>4</sub> / CMC at ratios 17/13/1/1 in a high shear mixer.

44 parts of the paste/phosphonate are mixed with 66 parts of the powder mixture.

The wet agglomerate is dried in a fluid bed dryer to an equilibrium relative humidity of about 12% at 20°C. The final agglomerate contains 30% anionic surfactant and 2% phosphonate and has an average particle size of about 500mm with less than 5% through Tyler 65. The bulk density of the agglomerates is 750g/L.

The mixture of the granular components has a bulk density of 780g/L and a particle size distribution as follows :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight of product on sieve</u>
14	1180	2
20	850	13
35	425	68
65	212	97
100	150	99

The mean particle size of the mixture of granular ingredients is about 525 micrometers.

The mixture of granular ingredients described above is placed inside a 600L rotating drum that operates at 15 rpm. A mixture of nonionic surfactant (C25E3) and a 20% aqueous solution of optical brightener (Pinopal CBS-X Trade Name, supplied by Ciba-Geigy) at ratios of 14:1, are sprayed onto the granular mixture while operating the drum to a level of 7%. The spraying time is about 7 minutes.

Immediately afterwards, perfume is sprayed on at a level of 0.5% while rotating the drum. Then, without stopping the rotation of the drum, zeolite is slowly added to the mixer to a level of about 8%, taking about 2 minutes. Once the addition of zeolite is finished, the mixer is allowed to rotate for about 30 seconds and is then stopped. The product is removed by opening the gate and further rotating the drum for about 10 seconds.

The product has a density after 2 days ageing of 910g/L.  
The particle size distribution is :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight of product on sieve</u>
14	1180	5
20	850	23
35	425	87
65	212	99
100	150	99.5

The mean particle size of the product is about 640 micrometers. This represents an increase in mean particle size of 22%.

The dispensing results of this product according to the method described in Section B is

Dispensing residue (%)	
2 L/min	24
3 L/min	2

The dissolution profile of the anionic surfactant, measured according to the method also described in Section B shows the time for dissolution of 50% of the anionic surfactant to be 1.8 minutes.

#### EXAMPLE II

A mixture of granular raw materials is prepared according to the following composition :

	<u>% by weight</u>
Anionic surfactant agglomerate	53.3
Granular silicate	3.2
Granular dense soda ash	11.0
Granular sodium citrate	18.1
Granular acrylic-maleic copolymer	7.9
Suds suppressor agglomerate	2.0
Enzymes	4.5
	-----
	100

The anionic surfactant agglomerate is prepared via agglomeration of a 78% active LAS/TAS/C35E<sub>3</sub>S 74:24:2 paste onto a powder mixture containing zeolite / carbonate / CMC at ratios of 20/10/1 in a high shear mixer. The wet agglomerate is dried in a fluid bed dryer to an equilibrium relative humidity of about 12% at 20°C. The final agglomerate contains 35% anionic surfactant, has an average particle size of 600 micrometers with 8% particles smaller than 212 micrometers and a bulk density of 740g/L.

The mixture of the granular components has a bulk density of 740g/L and the following particle size distribution :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight of product on sieve</u>
14	1180	5
20	850	17
35	425	66
65	212	97
100	150	99

The mean particle size of the mixture of granular ingredients is about 525 micrometers.

The above mixture (50kg) is placed in a Lödige FM 130 D. The shaft rotates at about 160 rpm and the chopper speed is 3000 rpm. A mixture of nonionic surfactant (C45E7) and 20% aqueous solution of an optical brightener at a ratio of

14:1 are sprayed onto the mixture of powders while both the shaft and the chopper are operated.

A total of 5.2kg of the liquid mixture is added in an interval of about 1 and a half minutes. Immediately after, 0.3kg of perfume is also sprayed on. Then 5kg of finely divided zeolite is added to the mixer. The addition time is about 2 minutes and after addition, the unit is operated without the chopper for another half a minute. The product is discharged through the opening in the bottom of the mixer.

The density of the product after 2 days is 897g/L. The particle size distribution is :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight of product on sieve</u>
14	1180	17
20	850	41
35	425	78
65	212	94
100	150	98

The mean particle size of the product is about 740 micrometers. This represents an increase in mean particle size of about 40%.

The dispensing results of this product according to the method described in Section B is

27

## Dispensing residue (%)

2 L/min 14

3 L/min 0

The dissolution profile of the anionic surfactant measured according to the method also described in Section B shows the time for dissolution of 50% of the anionic surfactant to be 1.0 minutes.

COMPARATIVE EXAMPLE III

A mixture of granular raw materials is prepared according to the following composition :

	<u>% by weight</u>
Anionic surfactant agglomerate	12.0
Blown powder	49.2
Silicate	3.2
Granular dense soda ash	11.0
Granular sodium citrate	18.1
Suds suppressor agglomerate	2.0
Enzymes	4.5
	-----
	100

The anionic surfactant agglomerate is prepared via dry neutralisation of acid LAS onto a powder mixture containing zeolite / carbonate at a ratio of 1/1 in a high shear mixer. The agglomerate contains 30% anionic surfactant, has an average particle size of 500 micrometers with 16% particles smaller than 212 micrometers and a bulk density of 740g/L.

The blown powder is made via spray-drying a mixture containing :

	<u>% by weight</u>
Anionic surfactant paste	40.0
Zeolite	44.0
Acrylic-maleic co-polymer	16.0

where the anionic surfactant paste is 50% surfactant active and contains LAS and TAS at ratios 2.4 :1.

The mixture of the raw material components has a bulk density of 670g/L and the following particle size distribution :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight</u> <u>of product on sieve</u>
14	1180	4
20	850	11
35	425	33
65	212	64
100	150	86

The mean particle size of the mixture of ingredients is about 370 micrometers.

The above mixture (50kg) is placed in a Lödige FM 130 D. The shaft rotates at about 160 rpm and the chopper speed is 3000 rpm. A mixture of nonionic surfactant (C45E7) and 20% aqueous solution of an optical brightener at a ratio of 14:1 are sprayed onto the mixture of powders while both the shaft and the chopper are operated.

A total of 5.2kg of the liquid mixture is added in an interval of about 1 and a half minutes. Immediately after, 0.3kg of perfume is also sprayed on. Then 5kg of finely divided zeolite is added to the mixer. The addition time is about 2 minutes and after addition, the unit is operated with the chopper for another 3 minutes. The product is discharged through the opening in the bottom of the mixer.

The density of the product after 2 days is 847g/L. The particle size distribution is :

<u>Tyler Sieve no.</u>	<u>micrometers</u>	<u>% by weight of product on sieve</u>
14	1180	7
20	850	13
35	425	47
65	212	75
100	150	88

The mean particle size of the product is about 400 micrometers.

The dispensing results of this product according to the method described in Section B is

Dispensing residue (%)

2 L/min	102
3 L/min	84

The dissolution profile of the anionic surfactant measured according to the method also described in Section B shows the time for dissolution of 50% of the anionic surfactant to be 0.8 minutes.

## Section B - Test Methods

### Rate of Dissolution of Anionic Surfactants under Stressed Conditions (Sotax Method)

#### Equipment

- 1) Sotax cup (1L)
- 2) Distilled water
- 3) Electrical stirrer motor with variable speed (IKA-Werk RW 20 DZM)
- 4) Stainless steel propeller stirrer (Sotax no 3990-2)
- 5) 6 disposable filter type units with pore size 0.22 micron (25 mm diam., Millex No. SLGS025NB Millipore).
- 6) Plastic syringes (2 mL) and disposable needles (21x 1½)
- 7) Sample collectors (15 mL glass tubes)
- 8) Set of Tyler sieves and sieving equipment (Rotap)
- 9) Thermostated bath

#### Sample Preparation

Take a representative sample of 10g of the detergent composition.

#### Experimental Procedure

- 1) Place the cup containing 1 L of water (or desired solution) in the bath at the desired temperature. Allow the temperature of the water to reach that of the bath.
- 2) Place the impeller in the cup at 33 mm from the bottom.
- 3) Prepare 5 syringes with a filter unit and a needle. Prepare 1 syringe with needle without the filter.
- 4) Set the mixer speed to 200 r.p.m.
- 5) Quickly add 10 g of the product to be tested. Start the stopwatch.
- 6) Remove, at precise intervals of 10 sec., 30 sec., 1 min., 2,5 min. and 5 min, about 2 mL samples with the

syringes. For adequate sampling, the needle has to be  $\pm$  4 cm below the surface of the liquid.

- 7) After taking the 5 min. sample, increase the speed of the impeller to 300 r.p.m.
- 8) After 10 minutes take another sample through the filter.
- 9) Take a sample of the liquid with the syringe without filter. The difference between the result of this and the previous one is an indication of the solubility that can be expected at this temperature. Care must be taken that during this time, the system does not increase its temperature due to the vigorous stirring action.
- 10) Carry out the analytical determination of the content of active ingredient (CatSO3 analysis or similar). When using a turbidimetric end point indication for the titration, care must be taken that there is no interference in the unfiltered sample due to the presence of insolubles.
- 11) Calculate the percent dissolved in each sample by using the unfiltered sample as 100 % (by CatSO3 analysis, even the undissolved surfactant will be titrated).
- 12) Plot the percent dissolved versus time for the first period of time (up to 5 min.). Calculate the percent solubility at the experimental conditions from the filtered sample at 10 min.

Dispensing under Stressed Conditions (Zanussi (TM) Method)

#### Equipment

- 1) Dispenser Zanussi shower type dispenser.  
The main wash compartment will be used.
- 2) Water City water.
- 3) Water Temperature  $20 \pm 1^\circ\text{C}$ .

- 4) Water Flow  $2 \pm 0.05$  L per  $60 \pm 1$  seconds.  
The test runs for 2 minutes. Calibrate the water flow rate using a measuring cylinder or similar receiver.
- 5) Sample Mass  $150 \pm 0.5$  g of the test product.

#### Experimental Procedure

- 1) Calibrate the equipment for above operating conditions.  
Ensure that the whole experimental rig is horizontal and that none of the nozzles of the dispenser are blocked.
- 2) Weigh the required amount of product to be tested in a cup. Ensure that the sample is representative of the entire product (avoid segregation when filling the cup).
- 3) Weigh the dispenser drawer after ensuring that it is properly dried.
- 4) Place a vertical positioning screen in the mainwash section of the dispenser, so that it blocks the width of the drawer at a distance of 12.5 cm from the end of the drawer furthest from the water exit. Pour the product into the dispenser between the vertical positioning screen and the end of the drawer furthest from the water exit. The powder should be poured in such a way as to keep the powder surface as level as possible. Remove the screen.
- 5) Place the dispenser drawer gently in its slot, ensuring it is fully home.
- 6) Start water at the calibrated flow rate. Ensure that water is flowing entirely in the mainwash compartment.
- 7) Stop the water flow after 2 minutes and wait until the water drain from the drawer is completely stopped.
- 8) Remove the drawer from the slot and drain any excess water by slight tilting of the drawer. Ensure that no product falls from the drawer. There should be no water in any other compartment of the drawer. If some water

is found, the system needs rechecking to ensure that all the water flow goes in the mainwash compartment.

- 9) Weigh the dispenser drawer with total residues.
- 10) Repeat the determination at least 5 times.
- 11) Average the wet residues. The result is expressed in %wt of the initial amount of dry product.

#### Accuracy and Assessment

Significant differences between products can be assessed when the average percent residues differ in 10% or more. A product is considered to show good dispensing profile if under this stressed test is below 30% residue at 2 L/min (and/or below 10% residue at 3 L/min).

What Is Claimed Is:

1. A process in which the bulk density of a particulate detergent material is increased starting from an initial bulk density of at least 600g/l, by spraying a liquid on to the particles and dusting with a fine powder in one or more rotating drum(s) or mixer(s), characterised in that the particulate detergent material initially has a mean particle size greater than 400 micrometers, and that the increase in the mean particle size during the process is not greater than 60%.
2. A process according to claim 1 such that the final bulk density of the particulate detergent material is greater than 750g/l, preferably greater than 800g/l.
3. A process according to either of claims 1 or 2 such that the initial particulate detergent material comprises organic detergent materials which have been processed into granules by method or methods other than spray drying.
4. A process according to any of the previous claims in which the liquid sprayed onto the particles comprises a nonionic surfactant at a level of up to 10% by weight of the finished product.
5. A process according to any of the previous claims in which at least one mixer is in the form of a horizontal cylinder comprising a rotating shaft along the axis of the cylinder, said shaft carrying mixing tools and said shaft rotating at a speed of less than 250rpm.
6. A process according to claim 5 in which the mixer also comprises cutters mounted on to one or more shafts, said shafts being radially mounted in the cylinder of the mixer,

and said shafts rotating at a speed of greater than 1000rpm.

7. A detergent composition having a bulk density of at least 750g/l, preferably at least 800g/l which comprises;

- a) From 5% to 20% of organic surfactant
  - b) From 5% to 20% of sodium aluminosilicate
- characterised in that the dispensing residue is less than 30% when:

a 150g sample of the detergent composition is poured into a drawer of a Zanussi (TM) shower-type dispenser, and 4 litres of water at a temperature of 20°C is passed through the said drawer from the nozzles of the dispenser at a rate of 2 litres/minute, after which the portion of the detergent composition remaining in said dispensing drawer is weighed, and the resulting weight expressed as a percentage of the initial 150g sample and averaged over at least 5 repetitions of the test, the resulting percentage being the dispensing residue.

and in that the rate of dissolution of the detergent composition is at least 50% of the sulphate/sulphonate salts passing into solution in less than 3 minutes when a 10g sample is dissolved in 1 litre of distilled water at a temperature of 20°C in a 1 litre Sotax cup, and with a Sotax stirring propellor no. 3990-2 rotating at 200rpm about a vertical axis, the bottom of the said stirring propellor being located 33mm above the bottom of the cup.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US93/08151

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : C11D 3/10; 3/12; 11/00; 17/00; 17/06.

US CL : 252/174, 174.14, 174.21, 174.25

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/174, 174.14, 174.21, 174.25

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)


Automated Patent System: High Density; High Bulk Density; High Apparent Density; High Active; Deterg?

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
<u>X</u> Y	US,A, 4,666,740 (Wixon) 19 May 1987. See col. 1, line 57-col. 2, line 9; col. 8, line 51-col. 9, line 41; Examples 4-5, especially col. 14, lines 19-34.	<u>1-3,7</u> 1-3,7
<u>X</u> Y	US,A, 5,030,379 (Knight et al) 09 July 1991. See col. 2, lines 13-44; col. 2, line 68-col. 3, line 2; col. 3, lines 23-34; Examples.	<u>1-3,7</u> 1-3,7
Y,P	US,A, 5,164,108 (Appel et al) 17 November 1992. See abstract; col. 7, lines 1-7 and lines 44-57; col. 9, lines 1-33 (Tables 3 and 4).	1-3, 7
A,P	US,A, 5,149,455 (Jacobs et al.) 22 September 1992. See entire document in general.	1-2,7

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 19 OCTOBER 1993	Date of mailing of the international search report 06 DEC 1993
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer  PAUL LIEBERMAN Telephone No. (703) 308-2520

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/08151

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 5,133,924 (Appel et al.) 28 July 1992. See abstract; col. 3, lines 60-64; col. 5, lines 34-44; Examples 1-8.	1-3,7
Y,P	US,A, 5,160,657 (Bortolotti et al.) 03 November 1992. See abstract; col. 3, lines 8-12; col. 4, lines 50-60; Examples 1-3	1-3,7